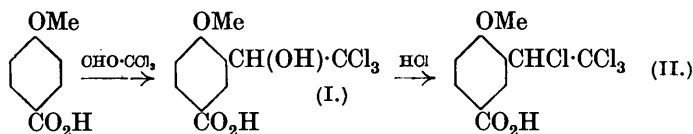


CCXLVI.—*The Condensation of Dichloroacetaldehyde with Anisic Acid and with p-Nitroanisole.*

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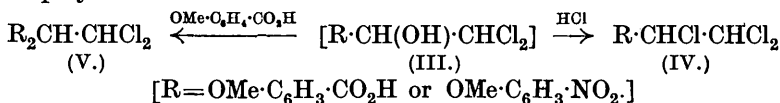
THE condensation of anisic acid with chloral in the presence of concentrated sulphuric acid (Chattaway and Calvet, J., 1928, 2913) gives 5-carboxy-2-methoxy-1- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethylbenzene (I), which can be isolated during the first stages of the reaction. If the reaction mixture, however, is saturated with hydrogen chloride and left for several days, 5-carboxy-2-methoxy-1- $\alpha\beta\beta\beta$ -tetrachloroethylbenzene (II) is produced.



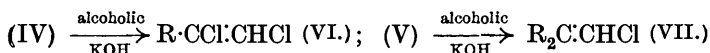
*p*-Nitroanisole condenses with chloral in a similar manner, but the

intermediate product, 5-nitro-2-methoxy-1- $\beta\beta$ -trichloro- $\alpha$ -hydroxyethylbenzene, has not been isolated.

Dichloroacetaldehyde, when similarly condensed with anisic acid in concentrated sulphuric acid saturated with hydrogen chloride, yields mainly 5-carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV; R = OMe·C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H) together with a small amount of  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V) (compare Baeyer, *Ber.*, 1872, 5, 25, 280, 1094; 1873, 6, 220; 1874, 7, 1181). In sulphuric acid not previously saturated with hydrogen chloride, the latter compound is the sole product. 5-Carboxy-2-methoxy-1- $\beta\beta$ -dichloro- $\alpha$ -hydroxyethylbenzene (III), which must be formed as an intermediate stage in both reactions, has not been isolated, being almost completely transformed into (IV) or (V) under the conditions employed.



5-Carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) and  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V) are colourless well-crystallised acids which yield corresponding *esters*, *acid chlorides*, *amides* and *anilides*. In both, the methoxy-group is very stable and is not easily affected by strong acids or alkalis. When heated with alcoholic potassium hydroxide, each loses a molecule of hydrogen chloride to form  $\alpha\beta$ -dichloro-5-carboxy-2-methoxystyrene (VI) and  $\beta$ -chlorodi-(5-carboxy-2-methoxyphenyl)ethylene (VII) respectively.

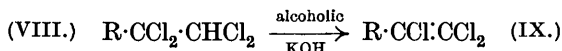


When oxidised by an alkaline solution of potassium permanganate, 5-carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) yields 4-methoxyisophthalic acid, a reaction which establishes the position of the entering group.

*p*-Nitroanisole condenses with dichloroacetaldehyde in a similar manner. With sulphuric acid alone,  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V; R = OMe·C<sub>6</sub>H<sub>3</sub>·NO<sub>2</sub>), and with sulphuric acid in the presence of hydrogen chloride, 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (as IV), are formed. When oxidised with potassium permanganate in boiling acetone, the latter yields 5-nitro-2-methoxybenzoic acid, showing that the -CHCl·CHCl<sub>2</sub> group occupies the ortho-position.

When refluxed with alcoholic potassium hydroxide,  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V) undergoes profound decomposition, but 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene

(IV) loses one molecule of hydrogen chloride and yields  $\alpha\beta$ -dichloro-5-nitro-2-methoxystyrene (VI). This compound combines directly with two atoms of chlorine, forming 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -tetrachloroethylbenzene (VIII), which, when heated with alcoholic potassium hydroxide, itself loses a molecule of hydrogen chloride to produce  $\alpha\beta\beta$ -trichloro-5-nitro-2-methoxystyrene (IX).



In the elimination of hydrogen chloride from 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV), the hydrogen atom must come from the  $\alpha$ -position and the chlorine from the  $\beta$ -position, since the dichloro-addition product of this unsaturated compound melts more than 30° lower than the other possible isomeride, 5-nitro-2-methoxy-1- $\alpha\beta\beta\beta$ -tetrachloroethylbenzene. The latter compound, formed by the action of *p*-nitroanisole upon chloral in the presence of concentrated sulphuric acid, also yields (IX) on treatment with alcoholic potassium hydroxide (Chattaway and Calvet, *loc. cit.*).

When 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) is dissolved in concentrated sulphuric acid and *p*-nitroanisole added,  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V) is slowly formed.

#### EXPERIMENTAL.

*Condensation of Anisic Acid with Dichloroacetaldehyde in the Presence of Sulphuric Acid saturated with Hydrogen Chloride.*—Dichloroacetaldehyde alcoholate (22.5 g.; 1 mol.) was slowly added, with vigorous shaking, to a solution of 20 g. of anisic acid in 200 c.c. of sulphuric acid to which 10 g. of sodium chloride had been added; a further considerable excess of sodium chloride was then added to ensure complete saturation with hydrogen chloride. After 1½ hours the mixture was poured over ice. The colourless solid obtained was fractionally crystallised from boiling alcohol, giving two products. The less readily soluble portion (1.2 g.) crystallised in compact prisms, m. p. 315°, and was shown to be  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V; R = OMe·C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>H), described below. The more soluble portion was 5-carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV), long slender flattened prisms (32 g.), m. p. 189—190° (Found: C, 42.2; H, 3.3; Cl, 37.4. C<sub>10</sub>H<sub>9</sub>O<sub>3</sub>Cl<sub>3</sub> requires C, 42.3; H, 3.2; Cl, 37.5%), very soluble in alcohol and glacial acetic acid, moderately easily soluble in ether and benzene, insoluble in light petroleum and water, and readily soluble in aqueous alkaline solutions.

*Condensation of Anisic Acid with Dichloroacetaldehyde in the Presence of Sulphuric Acid Alone.*—Anisic acid (20 g.; 2 mols.) was dissolved in 200 c.c. of concentrated sulphuric acid and 13.5 g. of

dichloroacetaldehyde alcoholate (1.3 mols.) were slowly added with shaking. After standing at 20° for 15 hours, the solution was poured over ice. The white precipitate of  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V) thus formed (26 g.) crystallised from acetic acid, in which it was quite soluble, in short compact prisms, m. p. 315° (Found : C, 54.2; H, 3.9; Cl, 17.6.  $C_{18}H_{16}O_6Cl_2$  requires C, 54.1; H, 4.0; Cl, 17.8%). This compound dissolves readily in aqueous alkalis, from which it may be precipitated unchanged by acids.

*Action of Alcoholic Potash on 5-Carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV).*—Alcoholic potash was added in excess to 10 g. of 5-carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene dissolved in 100 c.c. of alcohol. When the clear solution was heated, potassium chloride separated. On acidification with an excess of very dilute hydrochloric acid, a white precipitate of  $\alpha\beta$ -dichloro-5-carboxy-2-methoxystyrene (VI) came down, which crystallised from alcohol, in which it was moderately easily soluble, in bundles of long slender flattened prisms, m. p. 227—228° (Found : Cl, 28.6.  $C_{10}H_8O_3Cl_2$  requires Cl, 28.75%).

The trichloroethylbenzene (IV) was also heated nearly to boiling with concentrated aqueous sodium hydroxide, whereupon a thick precipitate of the sodium salt of  $\alpha\beta$ -dichloro-5-carboxy-2-methoxystyrene separated. It crystallised from alcohol, in which it was very soluble, in clusters of long slender needles which do not fuse at a high temperature. This compound, moderately easily soluble in hot water, was readily converted into the acid (VI), prepared above, by treating the aqueous solution with dilute hydrochloric acid.

*Preparation of the Ethyl Ester, Acid Chloride, and Amide of 5-Carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV).*—A solution of 10 g. of 5-carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) in 100 c.c. of ethyl alcohol containing several c.c. of concentrated hydrochloric acid was refluxed for 3½ hours. The resulting solution was concentrated and the ethyl ester which separated was crystallised from alcohol, in which it was extremely soluble, forming bundles of colourless needles, m. p. 69° (Found : Cl, 34.3.  $C_{12}H_{13}O_3Cl_3$  requires Cl, 34.15%). This ester was also readily obtained from the acid chloride, described below, by boiling with ethyl alcohol.

The acid chloride was produced when the acid (IV) was heated with phosphorus pentachloride. On pouring over ice, extraction with ether, and quick drying over anhydrous calcium chloride, a solution was obtained which yielded the acid chloride on concentration. It crystallised from light petroleum (b. p. 60—80°) in slender flattened prisms, m. p. 94° (Found : Cl, 47.2.  $C_{10}H_8O_2Cl_4$  requires Cl, 47.0%).

The *amide* was readily formed when the acid chloride was gently heated with a mixture of concentrated ammonia solution and alcohol. It crystallised from alcohol in clusters of long slender flattened prisms, m. p. 156° (Found: Cl, 37.8.  $C_{10}H_{10}O_2NCl_3$  requires Cl, 37.7%).

*Oxidation of 5-Carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) and Isolation of 4-Methoxyisophthalic Acid.*—5-Carboxy-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (10 g.) was dissolved in 300 c.c. of boiling water containing sodium carbonate in excess and to this solution were added about 9 g. of finely powdered potassium permanganate gradually until the colour persisted on continued boiling. The manganese dioxide was filtered off, and the colourless filtrate acidified with dilute hydrochloric acid; a white solid then separated. On crystallisation from acetic acid, 4-methoxyisophthalic acid, m. p. 275°, was obtained (Chattaway and Calvet, J., 1928, 2916).

*Action of Alcoholic Potash on  $\beta\beta$ -Dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V) with the Formation of the Ethylene Derivative (VII).*—The diphenylethane derivative (V) was dissolved in excess of alcoholic potash and refluxed for 10 hours. Potassium chloride separated and when the mixture was poured into an excess of very dilute hydrochloric acid,  $\beta$ -chloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethylene (VII) separated as a white solid. It crystallised from glacial acetic acid in small compact crystals, m. p. 339° (Found: Cl, 10.0.  $C_{18}H_{15}O_6Cl$  requires Cl, 9.8%), sparingly soluble in alcohol but more readily in glacial acetic acid.

*The Methyl and Ethyl Esters, Acid Chloride, Amide, and Anilide of  $\beta\beta$ -Dichloro- $\alpha\alpha$ -di-(5-carboxy-2-methoxyphenyl)ethane (V).*—The *ethyl* ester, prepared by refluxing for 15 hours an alcoholic suspension of the acid (V) to which several c.c. of concentrated hydrochloric acid had been added, and obtained by concentration of the resulting solution, crystallised from alcohol, in which it was very soluble, in flattened prisms, m. p. 117° (Found: Cl, 15.7.  $C_{22}H_{24}O_6Cl_2$  requires Cl, 15.6%). It was also obtained by boiling the acid chloride with ethyl alcohol.

The *methyl* ester, prepared by boiling the acid chloride with methyl alcohol, separated from methyl alcohol, in which it was quite soluble, in colourless slender flattened prisms, m. p. 154° (Found: Cl, 16.8.  $C_{20}H_{20}O_6Cl_2$  requires Cl, 16.6%).

Both esters are extremely difficult to hydrolyse and were recovered unchanged after boiling for several hours with aqueous sodium hydroxide solution.

The *acid chloride* was prepared in the usual manner by heating the acid (V) with phosphorus pentachloride. On pouring over ice, extraction with ether, and drying for 15 minutes over anhydrous

calcium chloride, the solution yielded the acid chloride on concentration. This crystallised from ether, in which it was quite soluble, in colourless hexagonal plates, m. p. 134° (Found: Cl, 32.4.  $C_{18}H_{14}O_4Cl_4$  requires Cl, 32.5%).

The *amide* was formed by gently heating the acid chloride with a mixture of concentrated aqueous ammonia and alcohol. It was moderately easily soluble in alcohol, from which it crystallised in quadrilateral plates, m. p. 257° (Found: Cl, 17.9; N, 7.0.  $C_{18}H_{18}O_4N_2Cl_2$  requires Cl, 17.7; N, 7.05%).

The *anilide* was obtained in a similar manner by heating the acid chloride with aniline. After treatment with dilute hydrochloric acid to dissolve the excess of aniline, the anilide separated from alcohol, in which it was moderately easily soluble, in colourless micro-crystals, m. p. 209° (Found: Cl, 12.8.  $C_{30}H_{26}O_4N_2Cl_2$  requires Cl, 12.9%).

*Condensation of p-Nitroanisole with Dichloroacetaldehyde in the Presence of Sulphuric Acid saturated with Hydrogen Chloride.*—To a solution of 15 g. of *p*-nitroanisole (1 mol.) in 150 c.c. of cold concentrated sulphuric acid were added 16 g. of dichloroacetaldehyde alcoholate (1 mol.), followed by 10 g. of sodium chloride. The mixture was thoroughly shaken and kept for 2 hours, more sodium chloride being added to ensure complete saturation with hydrogen chloride. A thick, apparently crystalline solid separated in the yellowish mixture, which was then poured over ice. A white solid was obtained, which, when fractionally crystallised from boiling alcohol, gave  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V; R=OMe·C<sub>6</sub>H<sub>3</sub>·NO<sub>2</sub>) (see below), slightly soluble, compact prisms (1 g.), m. p. 237°, and 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV), which crystallised from alcohol or glacial acetic acid, in which it was readily soluble, in colourless rectangular prisms, m. p. 140° (Found: Cl, 37.4.  $C_9H_8O_3NCl_3$  requires Cl, 37.4%).

*Condensation of p-Nitroanisole with Dichloroacetaldehyde in the Presence of Sulphuric Acid Alone.*—*p*-Nitroanisole (20 g.; 1 mol.) was dissolved in 200 c.c. of cold concentrated sulphuric acid and 10 g. of dichloroacetaldehyde alcoholate (1 mol.) were slowly added with shaking to the clear yellow solution. After 2½ hours, it was poured over ice, whereupon  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V) separated. It is easily soluble in acetic acid, less soluble in alcohol, and crystallises in colourless short compact prisms, m. p. 237° (Found: Cl, 18.0.  $C_{16}H_{14}O_6N_2Cl_2$  requires Cl, 17.7%).

*Action of Alcoholic Potash on 5-Nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV).*—When 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene, suspended in an excess of alcoholic potash, was heated to 60°, potassium chloride separated. Water was carefully added, and

a white precipitate of  $\alpha\beta$ -dichloro-5-nitro-2-methoxystyrene (VI) came down. This was very soluble in hot alcohol, from which it crystallised in clusters of colourless needles, m. p.  $66^\circ$  (Found: Cl, 28.4.  $C_9H_7O_3NCl_2$  requires Cl, 28.6%).

*Chlorination of  $\alpha\beta$ -Dichloro-5-nitro-2-methoxystyrene (VI).*—Chlorine was passed for  $\frac{1}{2}$  hour through a saturated solution of the styrene in acetic acid, whereupon the solution became warm and compact crystals separated. The product, 5-nitro-2-methoxy-1- $\alpha\alpha\beta\beta$ -tetrachloroethylbenzene (VIII), crystallised from glacial acetic acid, in which it was easily soluble, in colourless octahedra, m. p.  $165^\circ$  (Found: Cl, 44.2.  $C_9H_7O_3NCl_4$  requires Cl, 44.45%).

*Action of Alcoholic Potash on 5-Nitro-2-methoxy-1- $\alpha\alpha\beta\beta$ -tetrachloroethylbenzene (VIII).*—On heating this compound (VIII) with alcoholic potash in excess, potassium chloride was deposited. On careful addition of water,  $\alpha\beta\beta$ -trichloro-5-nitro-2-methoxystyrene (IX) separated as a white solid, which crystallised from acetic acid, in which it was easily soluble, in colourless plates, m. p.  $94^\circ$ , identical with the compound described by Chattaway and Calvet (J., 1928, 2917).

*Oxidation of 5-Nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV) and Isolation of 5-Nitro-2-methoxybenzoic Acid.*—To 5 g. of 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene dissolved in 100 c.c. of boiling acetone, potassium permanganate (25 g.) was added over a period of 30 hours. After 10 hours' boiling, the solid was separated from the cooled liquid and extracted with 100 c.c. of alcohol. On concentration of this solution, needles of potassium 5-nitro-2-methoxybenzoate separated, from which 5-nitro-2-methoxybenzoic acid was obtained on acidification, m. p.  $161^\circ$  (Chattaway and Calvet, *loc. cit.*).

*Action of p-Nitroanisole upon 5-Nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene (IV), in the Presence of Concentrated Sulphuric Acid with the Formation of  $\beta\beta$ -Dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane (V).*—To a solution of 6 g. of *p*-nitroanisole in 60 c.c. of concentrated sulphuric acid was added a suspension of 10 g. of 5-nitro-2-methoxy-1- $\alpha\beta\beta$ -trichloroethylbenzene in 60 c.c. of sulphuric acid. This mixture was shaken at intervals during 20 hours. Hydrogen chloride was evolved, but the initial material did not dissolve completely. The solution was filtered and poured over ice whereupon a solid separated which contained, besides uncombined *p*-nitroanisole,  $\beta\beta$ -dichloro- $\alpha\alpha$ -di-(5-nitro-2-methoxyphenyl)ethane, m. p.  $237^\circ$ , identical with the compound described above.